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Two-Electron Redox Chemistry and Reversible Umpolung of a Gold–Antimony Bond**

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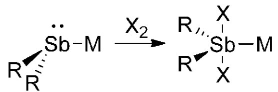
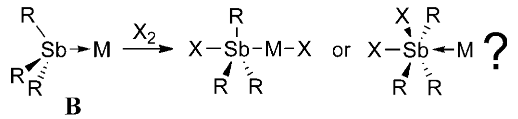
Two-electron redox processes occurring at the core of dinuclear metal complexes are important because of their implication in a number of chemical transformations ranging from the photocatalytic production of dihydrogen[1] to the oxidative functionalization of C–H bonds.[2] Two-electron redox processes are also well documented for binuclear gold complexes[3] as well as for gold/rhodium,[4] gold/iridium[5] and gold/platinum[6] heterobimetallic complexes. One of the common features displayed by all of these complexes relates to their ability to sustain two-electron redox chemistry without decomposition of the bimetallic core. As part of our interest in fundamental aspects of main-group chemistry, we have recently questioned whether similar processes could also be observed at the bimetallic core of main-group/transition-metal complexes.

Triarylstibines are soft σ-donor ligands which have been incorporated in a variety of late transition-metal complexes.[7] They are also well known to undergo facile two-electron oxidation when exposed to oxidizing agents such as halogens.[8] While there is precedent for dialkylstibido transition-metal compounds (type **A**) to undergo oxidative addition at the antimony center,[9] no analogous reactivity has been reported for stibine metal complexes of type **B**. With the discovery of main-group-based, two-electron redox platforms in mind, we have now decided to study the synthesis and oxidation of complexes of type **B**. Herein, we report the first incarnation of this idea in the case of a gold–antimony compound.

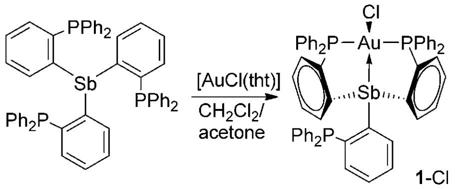


A



B

To prevent dissociation of the gold–antimony bimetallic core upon oxidation, we chose to work with a stibine ligand whose interaction with the gold center would be supported by pendant donor ligands. These considerations led us to focus on the triphosphanylstibine ligand [(o-(Ph_2P)C_6H_4)$_3$Sb] (referred to as L)[10] which was allowed to react with [AuCl(tht)] in CH_2Cl_2/acetone to produce **1**-Cl as a pale yellow precipitate (Scheme 1). At −55 °C in $CDCl_3$, the $^{31}P\{^1H\}$ NMR spectrum of **1**-Cl displays two signals at $\delta = +39.5$ and −7.4 ppm in a 2:1 intensity ratio thus suggesting that only two of the three phosphine arms of the ligand are coordinated to the gold atom. Upon elevation of the temperature, these two peaks coalesce into one signal at $\delta = +24.4$ ppm indicating the onset of a rapid exchange. Line shape analysis of the $^{31}P\{^1H\}$ NMR spectra of **1**-Cl over the −55 °C–+22 °C temperature range followed by an Eyring analysis afforded $\Delta H^{\ddagger} = +16.7$ ($\pm$ 0.9) kcal mol^{-1} and $\Delta S^{\ddagger} = +16.6(\pm 3.8)$ cal mol^{-11} K^{-11}, suggesting a dissociative exchange of the phosphine arms. The ESI mass spectrum of this complex shows a peak at m/z 1101.1180 amu corresponding to the [LAu]$^+$ ion. A final clarification of the structure of this compound was derived from a single-crystal diffraction study which confirmed the coordination of two of the phosphorus atoms to the gold chloride fragment (Figure 1).[11] Inspection of the P-Au-P and P-Au-Cl angles ($\Sigma = 359.46°$) shows that these primary ligands are arranged around the gold atom in a trigonal planar fashion. Further inspection of the structure reveals a Au1–Sb1 separation of 2.8374(4) Å. This separation is longer than the Au–Sb bond distances found in complexes such as [Au($SbPh_3$)$_4$][ClO_4] (2.656–2.658 Å)[12] and [Au(μ_2-1,8-($C_{10}H_6$))$_2$$SbPh_2$] (2.76 Å av.).[13] Another noteworthy feature is the value of the Au1-Sb1-C37 angle (164.80(11)°) which indicates that the stibine ligand approaches the gold atom to achieve a seesaw rather than a tetrahedral geometry.



Scheme 1. Synthesis of complex **1**-Cl. (tht = tetrahydrothiophene).

With compound **1**-Cl in hand, we sought to determine if the gold antimony core could sustain oxidation. To this end, **1**-Cl was allowed to react with $PhICl_2$ in CH_2Cl_2 resulting in the

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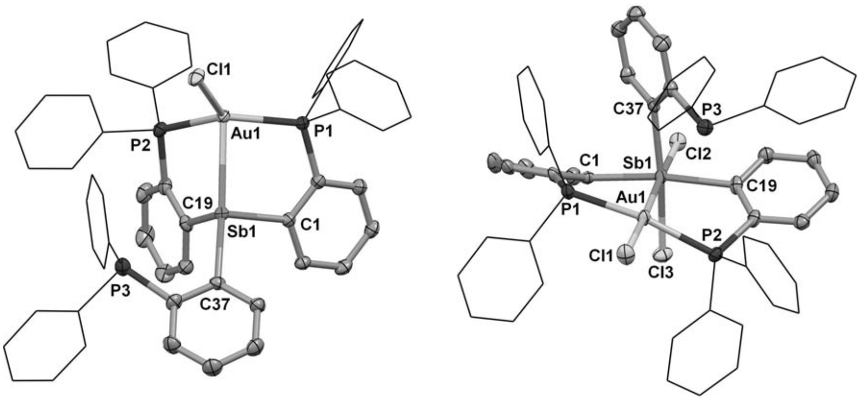
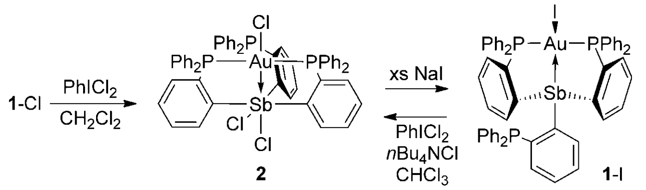


Figure 1. Crystal structures of **1**-Cl (left) and **2** (right). Thermal ellipsoids are set at 50% probability. Phenyl groups are drawn in wireframe and hydrogen atoms are omitted for clarity. Pertinent metrical parameters can be found in the text.



Scheme 2. Synthesis of complex **2** and its conversion into **1**-I.

formation of complex **2** as a yellow, air stable derivative (Scheme 2). The ESI mass spectrum of **2**, which displays a peak corresponding to the $[LCl_2Au]^+$ ion (m/z 1171.0551 amu), provided initial evidence for the oxidative addition of chlorine. The $^{31}P\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ shows a single resonance at $\delta = 41.9$ ppm, which in light of the crystal structure of **2** (see Figure 1), indicates a rapid exchange of the phosphine arms on the NMR time scale. This signal showed no tendency toward decoalescence upon cooling to −50 °C. Accordingly, the ^1H NMR ($CDCl_3$) exhibits a single downfield doublet at $\delta = 8.25$ ppm corresponding to the phenylene proton *ortho* to antimony. The crystal structure of **2**, which shows that only two phosphine arms are coordinated to the gold center, also confirms addition of a Cl_2 molecule to the antimony center.[11] While it is tempting to argue that oxidation is limited to the antimony center, the dinuclear core of the structure shows a clear response to oxidation. In particular, the Au–Sb distance in **2** (2.7086(9) Å) is shorter than that measured for **1**-Cl. Changes are also observed in the coordination sphere of the metals which adopt a distorted octahedral and square planar geometry for antimony and gold, respectively. These changes, and in particular the square planar geometry of the gold atom, indicate that the latter is affected by oxidation as it transitions from a monovalent form in **1**-Cl to trivalent form in **2**.

To better understand the changes induced by oxidation, the structures of **1**-Cl and **2** have been optimized using DFT methods (ADF: BP86/TZP with ZORA) and subjected to a Boys localization analysis and an NBO analysis (Gaussian: BP86 with 6-31g for H, C; 6-311g(d) for P, Cl; and CRENBS ECP for Sb, Au). For **1**-Cl, the NBO analysis identifies a relatively weak lp(Sb)→p(Au) donor–acceptor interaction ($E_{\text{del}} = 35.28$ kcal mol^{-1}) as the primary interaction (Figure 2). Accordingly, the Boys orbital corresponding to this interaction is localized on antimony with only a slight polarization toward the gold atom supporting a rather weak dative bond (Figure 2). For **2**, NBO analysis indicates that Au–Sb bonding is dominated by Au→Sb donation.[14] The interactions identified include a lp(Au)→σ*(Sb-Cl) as well as two lp(Au)→σ*(Sb-C) interactions, whose concomitant deletion give rise to an increase of the energy of the complex by $E_{\text{del}} = 63.59$ kcal mol^{-1} (Figure 2). These computational results support a strengthening of the Au–Sb bond on going from **1**-Cl to **2**. They also indicate an umpolung of the Au–Sb dative bond which switches from Sb→Au in **1**-Cl to Au→Sb in **2**. This umpolung is consistent with a transition of the gold atom from monovalent in **1**-Cl to trivalent in **2**. This view is validated by the results of the Boys localization analysis which identifies a Au–Sb σ-bond that clearly engages both metal atoms (Figure 2). Complex **2** is related to a series of complexes with gold–Lewis acid interactions[15] pioneered by Bourissou and co-workers.[16] Such complexes have typically been assembled by coordination of phosphine/Lewis acid ambiphilic ligands to gold(I) synthons. In this respect, the synthesis of **2** stands out because it is achieved by oxidation of a pre-assembled complex.[17]

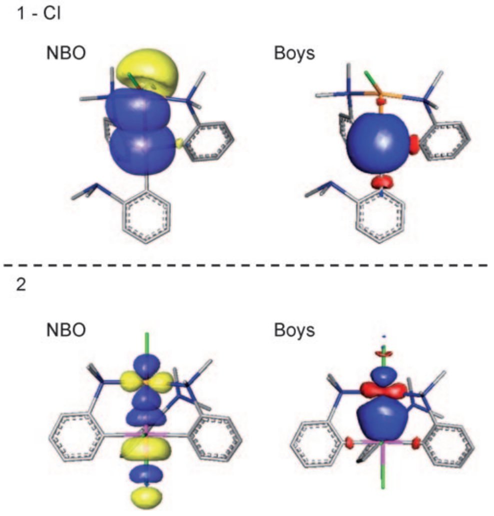


Figure 2. Plots of the primary Au–Sb Boys orbitals (0.03 isodensity value) and NBO donor–acceptor interactions in **1**-Cl and **2**. Hydrogen atoms and phenyl rings have been omitted for clarity.

To conclude this study, it became important for us to address the reversibility of the redox process supported by this new dinuclear platform. Having already shown that **1** can be cleanly oxidized into **2**, we decided to test the reverse reaction. While we found that **2** did not cleanly react with strong reducing agents such as Na or Na/Hg, we observed a clean reaction in the presence of NaI. Indeed, upon mixing **2** with 4 equiv of NaI in acetone, the solution quickly developed a brown color assigned to the formation of I_3^- (Scheme 2). The reaction could be conveniently followed by ^{31}P NMR spectroscopy which clearly indicates formation of a new species featuring a broad resonance at $\delta = +22.7$ ppm. Reduction of **2** is supported by the ESI mass spectrum of the reaction mixture which exhibits a peak corresponding to the $[LAu]^+$ ion ($m/z = 1101.1188$). The product of this reaction has been isolated in 63 % yield and unambiguously identified as **1**-I using conventional characterization means. Single crystal X-ray diffraction indicates that the structure of **1**-I is close to that of **1**-Cl as indicated by the similarity of the Au–Sb bonds (2.7958(11) Å in **1**-I vs. 2.8374(4) Å in **1**-Cl). Lastly, **1**-I can be reoxidized into **2** by reaction with $PhICl_2$ in the presence of excess $n\mathrm{Bu_4NCl}$ in $CHCl_3$ as indicated by ^{31}P NMR and ESI MS monitoring of the reaction.[18]

In summary, we report a gold–antimony compound whose binuclear core sustains reversible two-electron redox chemistry. This reversible process induces an umpolung of the Sb–Au dative bond which switches from Sb→Au in the reduced state to Au→Sb in the oxidized state. This easily triggered and reversible umpolung constitutes a promising way to tune the reactivity of the transition-metal center, an aspect that we are currently investigating.

Experimental Section

General considerations: ***Antimony compounds are highly toxic and should be handled cautiously.*** $SbCl_3$ was purchased from Alfa Aesar, NaI was purchased from Aldrich, and both were used as received. The ligand $[(o\text{-}(Ph_2P)C_6H_4)_3Sb]$,[10] $PhICl_2$,[19] and [(tht)AuCl][20] (tht = tetrahydrothiophene) were prepared according to the reported procedures. All air and moisture sensitive manipulations were carried out under an atmosphere of dry N_2 employing either a glove box or standard Schlenk techniques. Pentane and CH_2Cl_2 were dried by passing through an alumina column. All other solvents were used as received. Ambient temperature NMR spectra were recorded on a Varian Unity Inova 400 FT NMR (399.59 MHz for ^{1}H, 161.74 MHz for ^{31}P, 100.45 MHz for ^{13}C) spectrometer. Low-temperature ^{31}P{^{1}H} NMR spectra were recorded on a Varian Inova 300 FT NMR spectrometer (121.42 MHz for ^{31}P). Chemical shifts are given in ppm, and are referenced to residual ^{1}H and ^{13}C solvent signals and external H_3PO_4 for ^{31}P. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). Electrospray mass spectra were obtained with a SciexQstarr Pulsar and a Protana Nanospray ion source.

1-Cl: A solution of [AuCl(tht)] (35 mg, 0.110 mmol) in acetone (2 mL) was added dropwise to a solution of $[(o\text{-}C_6H_4P(PPh_2))_3Sb]$ (100 mg, 0.1 mmol) in acetone/CH_2Cl_2 (5:1 mL) at ambient temperature. The resulting yellow solution was allowed to stir for 15 min after which time a pale yellow precipitate began to form. Pentane (10 mL) was added to complete precipitation of the product. The precipitate was collected by filtration and washed with pentane (3 × 3 mL) and dried in vacuo to afford 105 mg (83 %) of **1**-Cl as a pale yellow powder. Single crystals of **1**-Cl·acetone suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a solution of the compound in acetone. ^{1}H NMR (399.59 MHz; $CDCl_3$): $\delta = 7.10$–7.17 (m, 9 H, PPh-C*H*), 7.27–7.32 (m, 18 H, PPh-C*H*), 7.39–7.46 (m, 12 H, PPh-C*H*), 7.67 ppm (d, 3 H, $o\text{-}P(Sb)C_6H_4$, $^3J_{H\text{-}H} = 6.96$ Hz). ^{13}C NMR (100.45 MHz; $CDCl_3$): $\delta = 128.35$ (bs, CH_{Ph}), 128.54 (bs, CH_{Ph}), 129.88 (bs, CH_{Ph}), 130.33 (bs, CH_{Ph}), 133.33 (pseudo-quart, $o\text{-}P(Sb)C_6H_4$, $J_{C\text{-}P} = 10.17$ Hz), 133.72 (bs, CH_{Ph}), 133.97 (pseudo-quart, $o\text{-}P\text{-}CH_{Ph}$, $J_{C\text{-}P} = 5.34$ Hz), 137.21 (pseudo-quart, $P\text{-}C_{Ph\ ipso}$, $J_{C\text{-}P} = 5.33$ Hz), 140.33 (pseudo-quart, $Sb\text{-}C_{ipso}$, $J_{C\text{-}P} = 11.70$ Hz), 150.95 ppm (pseudo-quart, $P\text{-}C_{ipso}$, $J_{C\text{-}P} = 22.38$ Hz). ^{31}P{^{1}H} NMR (161.74 MHz; $CDCl_3$): $\delta = 24.4$ ppm. HRMS: *m*/*z* calcd for $C_{54}H_{42}AuP_3Sb^+$: 1101.1203, found: 1101.1180. Elemental analysis calcd (%) for $C_{54}H_{42}AuClP_3Sb + C_3H_6O$: C 57.24, H 4.04; found: C 56.50, H 4.24 (approx. 1 equiv of acetone was lost in drying).

2: A solution of $PhICl_2$ (60 mg, 0.22 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a solution of **1**-Cl (250 mg, 0.22 mmol) in CH_2Cl_2 (5 mL) at ambient temperature. The reaction was stirred for 20 min. before removing the solvent in vacuo. The resulting yellow solid was washed with acetone (2 × 2 mL) and pentane (2 × 3 mL) and dried in vacuo to afford 195 mg (73 %) of **2** as a yellow powder. Single crystals of **2**·2 CH_2Cl_2 suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a solution of the compound in CH_2Cl_2. ^{1}H NMR (399.59 MHz; $CDCl_3$): $\delta = 6.88$ (m, 3 H, $o\text{-}P(Sb)C_6H_4$), 7.19–7.36 (m, 36 H, Ph-C*H*), 8.25 (d, 3 H, Ph-C*H*, $^3J_{H\text{-}H} = 7.87$ Hz). ^{13}C NMR (100.45 MHz; $CDCl_3$): $\delta = 128.69$ (bm, CH_{Ph}), 128.98 (bs, CH_{Ph}), 130.56 (bm, $Sb\text{-}C_{ipso}$), 131.60 (bs, CH_{Ph}), 131.81 ((bs, CH_{Ph}), 132.36 (bs, CH_{Ph}), 133.77 (bd, $CH_{Phortho}$, $^2J_{C\text{-}P} = 4.58$ Hz), 134.11 (bs, CH_{Ph}), 136.53 (bd, $P\text{-}C_{Ph\,ipso}$, $^1J_{C\text{-}P} = 5.38$ Hz), 154.64 ppm (bm, $P\text{-}C_{ipso}$). ^{31}P{^{1}H} NMR (161.74 MHz; $CDCl_3$): $\delta = 41.91$ ppm. HRMS: *m*/*z* calcd for $C_{54}H_{42}AuCl_2P_3Sb^+$: 1171.0580, found: 1171.0551. Elemental analysis calcd (%) for $C_{54}H_{42}AuCl_3P_3Sb + 2\,CH_2Cl_2$: C 48.78, H 3.36; found: C 48.06, H 3.34 (approx. 1 equiv of CH_2Cl_2 was lost in drying).

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